



# Earth-abundant Ni<sub>2</sub>P/g-C<sub>3</sub>N<sub>4</sub> lamellar nanohydrids for enhanced photocatalytic hydrogen evolution and bacterial inactivation under visible light irradiation

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## ABSTRACT

Photocatalysts made of earth-abundant elements are highly desired for photocatalytic H<sub>2</sub> evolution as well as bacterial inactivation without requirement of noble metal (i.e. Pt, Ag). In this study, nickel phosphide (Ni<sub>2</sub>P) was used as a nonprecious co-catalyst to couple with metal-free g-C<sub>3</sub>N<sub>4</sub> based on Z-scheme type of electron transportation model. The exfoliation of bulk g-C<sub>3</sub>N<sub>4</sub>, the *in-situ* synthesis and anchoring of Ni<sub>2</sub>P nanoparticles onto the g-C<sub>3</sub>N<sub>4</sub> nanosheets were achieved in one-step by a hydrothermal method without adding any surfactants or templates. The optimized Ni<sub>2</sub>P/g-C<sub>3</sub>N<sub>4</sub> lamellar nanohydrids exhibited remarkably enhanced visible-light-driven photocatalytic activity for H<sub>2</sub> evolution and bacterial inactivation without noble metal loading, and the obtained activity is approximately 22 and 10 times higher than that of pure g-C<sub>3</sub>N<sub>4</sub>, respectively. The Ni<sub>2</sub>P was proposed to effectively trap the photo-generated e<sup>-</sup> via a Z-scheme type of route, thus significantly promoting the e<sup>-</sup>-h<sup>+</sup> separation and subsequent reduction of protons to generate H<sub>2</sub>. The bacterial inactivation was found to undergo a direct h<sup>+</sup> oxidation process, and therefore the trapping of e<sup>-</sup> by Ni<sub>2</sub>P also facilitated h<sup>+</sup> accumulation, leading to enhanced bacterial inactivation efficiency. This study demonstrates a proof-of-concept for constructing all-earth-abundant photocatalysts without any noble metal elements for both energy production and environmental application.

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## 1. Introduction

Energy crisis and environmental pollution are two of the major problems facing the human society. Among the numerous energy carriers, H<sub>2</sub> is considered to be one of the most ideal alternative candidates for the replacement of fossil fuels [1]. Since water is abundant on the Earth and it contains 11.1% hydrogen in weight, the most promising and simplest way for H<sub>2</sub> production is to liberate hydrogen from water. Therefore, photocatalytic H<sub>2</sub> production from water has attracted much attention as a potential method to convert and store inexhaustible solar energy as chemical

energy, thus solving the energy crisis problems [2,3]. Meanwhile, the elimination of pathogenic microorganisms, such as bacteria, viruses and fungi in water environments, has been one of the major tasks for wastewater treatment, as waterborne diseases have been estimated to cause 80% of illnesses in the developing country [4]. However, current water disinfection methods, such as chlorination, ozonation, and UV disinfection, have inevitable disadvantages, including secondary pollution, recolonization, safety concerns, and especially energy-consuming problems, which is unfavorable for long-term sustainable development [5,6]. Therefore, photocatalysis has also been regarded as an alternative disinfection method due to its direct utilization of solar energy to drive the microorganism inactivation process, thus accomplishing a “green”, mild and low-cost water disinfection process.

Since the pioneer report of photocatalytic H<sub>2</sub> production and bacterial inactivation in 1972 [7] and 1985 [8], respectively, much

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efforts have been devoted to the rational design and synthesis of inorganic semiconductors with high quantum efficiency. Among these catalytic materials,  $\text{TiO}_2$  is the most widely investigated photocatalyst. However, the application of  $\text{TiO}_2$  is limited by the large band gap energy of 3.2 eV, only excited with UV-light which accounts for less than 5% of the solar spectrum. Meanwhile, non- $\text{TiO}_2$  based semiconductors as visible-light-driven (VLD) photocatalysts has also been actively investigated, such as metal oxides [9,10], sulfides [11,12] and oxynitrides [13]. In most work reported so far, co-catalysts loaded on the surface of semiconductor are needed to enhance the photocatalytic activity. For example, Pt is indispensable for  $\text{H}_2$  evolution to promote the separation of photoexcited charge carriers and reduce the over-potential. On the other hand, Ag element was found to play an important role in bacterial inactivation due to its excellent electron trapping ability and localized surface plasmon resonance (LSPR) effects [14]. However, the scarcity and high cost of these noble metals significantly hamper their practical and large-scale applications. Therefore, the development of novel active catalysts that are made of inexpensive earth-abundant materials is highly desirable both from environmental friendly and economic point of view.

A typical case of such earth-abundant photocatalysts is the emerged graphitic carbon nitride ( $\text{g-C}_3\text{N}_4$ ) polymer which can be synthesized simply by thermal calcinations [15]. It has been demonstrated to be able to catalyze a variety of photoredox reactions, such as water splitting [16],  $\text{CO}_2$  reduction [17], organics degradation [18], and bacterial inactivation [19], under visible light (VL) irradiation. However, the pristine  $\text{g-C}_3\text{N}_4$  suffers from a high recombination rate of photoexcited charge carriers (i.e.  $e^-$  and  $h^+$ ) as well as low photocatalytic activity [20]. A series of strategies were therefore developed to modify this metal-free catalyst, for instance by nanostructure engineering [21], metallic/nonmetallic heteroatom doping [22], crystal structure engineering [23], and heterostructure construction [24]. Le et al. has employed a hard-templating method to fabricate Cu-doped mesoporous  $\text{g-C}_3\text{N}_4$ , which showed 2 times higher photocatalytic degradation activity than that of pure  $\text{g-C}_3\text{N}_4$  [25]. In addition,  $\text{ZnO/g-C}_3\text{N}_4$  mesoporous nanocomposite has also been synthesized by similar method and found to exhibit much enhanced photocatalytic activity than that of pure  $\text{mpg-C}_3\text{N}_4$  and  $\text{ZnO}$  under VL irradiation [26]. Although concrete progress has been made to enhance the photocatalytic activity of  $\text{g-C}_3\text{N}_4$ , most of these efforts still need noble metals (i.e. Pt) as co-catalysts especially for  $\text{H}_2$  production. Therefore, it is very attractive to develop  $\text{g-C}_3\text{N}_4$  based photocatalysts without noble metal(s), thus a genuine earth-abundant photocatalytic systems can be achieved for both  $\text{H}_2$  production and bacterial inactivation.

Nickel phosphides comprised of inexpensive and earth-abundant elements have garnered a lot of recent interest due to their unique optoelectronic properties and potential applications [27], such as hydrodesulfurization [28], hydrodenitrification [29] and electrochemical hydrogen evolution reactions, where they benefit from low over-potentials and the largest cathodic densities among non-noble metal catalysts [30–32]. Very recently, the use of  $\text{Ni}_2\text{P}$  nanocrystals as co-catalysts was frequently extended to  $\text{H}_2$  evolution by semiconductor photocatalysts, such as  $\text{CdS}$  [33,34],  $\text{TiO}_2$  [35] and  $\text{g-C}_3\text{N}_4$  [36], representing a rising star for the replacement of Pt as the next generation earth-abundant co-catalysts. However, these composite photocatalysts were synthesized with complicated multistep methods, or using toxic white phosphorus as the precursors, which significantly constraints their practical application. In addition, no previous study has evaluated the performances of metal phosphide as a co-catalyst for bacterial inactivation.

Herein, the first study of using metal phosphide as a non-precious co-catalyst with  $\text{g-C}_3\text{N}_4$  was demonstrated for both  $\text{H}_2$  evolution and bacterial inactivation. The  $\text{Ni}_2\text{P}/\text{g-C}_3\text{N}_4$  lamellar

nanohydrids photocatalyst was synthesized for the first time by one-pot hydrothermal method with *in-situ* anchoring of  $\text{Ni}_2\text{P}$  nanocrystals onto the exfoliated  $\text{g-C}_3\text{N}_4$  nanosheets, using red phosphorus as a “green”, cheap and easy-to-handle precursor. The as-prepared  $\text{Ni}_2\text{P}/\text{g-C}_3\text{N}_4$  photocatalyst exhibited high photocatalytic activity in  $\text{H}_2$  evolution and bacterial inactivation without noble metal loading under visible light irradiation. The loading amount of  $\text{Ni}_2\text{P}$  was optimized and the photocatalytic mechanisms were also investigated in detail. This work creates an avenue not only for the development of earth-abundant photocatalysts, but also for the use of metal phosphide as nonprecious co-catalysts for cost-effective  $\text{H}_2$  production as well as water disinfection.

## 2. Experimental

### 2.1. Sample preparation

All chemicals were purchased in analytical grade and used without further purification. Bulk  $\text{g-C}_3\text{N}_4$  was synthesized following the previous reference [37]. In a typical procedure, 10 g melamine was heated at 550 °C for 4 h in static air with a heating rate of 2.3 °C min<sup>-1</sup>. After cooling, the resultant yellow agglomerates were milled into powder in an agate mortar for further use.

The  $\text{Ni}_2\text{P}/\text{g-C}_3\text{N}_4$  was synthesized by a one-pot hydrothermal method using red phosphorus (red P),  $\text{NiCl}_2$  and  $\text{g-C}_3\text{N}_4$  as the starting materials. Typically, 0.3 g bulk  $\text{g-C}_3\text{N}_4$  powder, a calculated  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  and red P (weight ratio = 0.95:0.7) were mixed into 20 mL deionized water. The weight ratio of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  to red P is determined according to the previous literature [38]. The mixture was stirred for 20 min at room temperature (ca. 25 °C) and then transferred to a 25 mL Teflon stainless steel autoclave, then sealed and maintained at 140 °C for 12 h in an air dry oven. When the autoclave was cooled to room temperature, the resulting product was collected and washed with distilled water and absolute ethanol for several times. The obtained samples were dried in vacuum at 60 °C for 12 h. The as-fabricated samples are denoted as x wt%  $\text{Ni}_2\text{P}/\text{g-C}_3\text{N}_4$ , where “x” stands for the weight content of  $\text{Ni}_2\text{P}$ . As a reference, pure  $\text{Ni}_2\text{P}$  was also prepared as control using the same method [38].

### 2.2. Catalysts characterization

X-ray diffraction (XRD) patterns of the samples were recorded with a Rigaku Smart Lab X-ray diffractometer using  $\text{Cu K}\alpha 1$  irradiation ( $\lambda = 1.5406 \text{ \AA}$ ). The accelerating voltage and applied current were 40 kV and 40 mA, respectively. UV-vis diffuse reflectance spectrum (UV-vis DRS) was obtained for the dry-pressed disk sample using a Varian Cary 500 UV-vis spectrophotometer equipped with a labsphere diffuse reflectance accessory.  $\text{BaSO}_4$  was used as a reflectance standard in the UV-vis DRS experiment. The morphology of the prepared materials was characterized by scanning electron microscopy (FESEM, FEI, Quanta 400 FEG) and transmission electron microscopy (TEM, FEI Tecnai G2 Spirit). The structure of composites was characterized by a Fourier transform infrared spectrometer (FT-IR, Nicolet 670) at a resolution of 4 cm<sup>-1</sup>. The surface electronic states were analyzed by X-ray photoelectron spectroscopy (XPS, PerkinElmer PHI 5000). All the binding energy values were calibrated by using C1s = 284.6 eV as a reference. Photoluminescence spectra (PL) of the samples were obtained at room temperature excited by incident light of 375 nm [39] using a Hitachi F-4500 fluorescence spectrophotometer.

Photocurrent measurements were carried out on an electrochemical workstation (CHI 660D, Shanghai Chen Hua Instrument Company, China) with a conventional three electrode cell, using a Pt plate and a saturated Ag/AgCl electrode as counter electrode

and reference electrode, respectively. The working electrode was prepared on indium-tin oxide (ITO) glasses, which was cleaned by sonication in chloroform, acetone and ethanol for 30 min, respectively. The glass was then rinsed with water and kept in isopropanol for 24 h. Five-milligrams of samples and 10  $\mu\text{L}$  of Nafion solution (5 wt%) were dispersed in a 1 mL water/isopropanol mixed solvent (3:1 v/v) by sonication to form a homogeneous catalyst colloid. Then, 100  $\mu\text{L}$  of the catalyst colloid was deposited onto the ITO glass with areas of approximately 1  $\text{cm}^2$ . The working electrodes were immersed in a 0.1 M  $\text{Na}_2\text{SO}_4$  aqueous solution without additive for 30 s before the measurement was carried out.

### 2.3. Photocatalytic $\text{H}_2$ evolution

The photocatalytic  $\text{H}_2$  evolution experiments were carried out in a Pyrex reaction cell connected to a closed gas circulation and evacuation system. 40 mg of photocatalyst was dispersed in 50 mL of aqueous solution containing 10 vol% triethanolamine (TEOA) as a sacrificial agent. The suspension was purged with argon gas to remove dissolved air before irradiation. The solution was irradiated by a 300 W Xenon lamp (Beijing Perfect Light Co. Ltd., Beijing) equipped with a 420 nm cut-off filter. The amount of  $\text{H}_2$  generated from photocatalytic water splitting was measured by Techcomp GC7900 gas chromatography with TCD detector and a capillary column (molecular sieve 5 Å). High purity nitrogen gas was used as a carrier gas. Wavelength dependence of  $\text{H}_2$  evolution rate was measured by using an appropriate band pass filter (420, 450 and 550, respectively). The intensity of the monochromatic light was averaged at 5 representative points by a light meter (LI-COR, USA) and the active area of the reactor was approximately 38.5  $\text{cm}^2$ . The apparent quantum efficiency (AQE) was measured and calculated according to the following Eq. (1):

$$\begin{aligned} \text{AQE} [\%] &= \frac{\text{number of reacted electrons}}{\text{number of incident photons}} \times 100 \\ &= \frac{\text{number of evolved H}_2 \text{ molecules} \times 2}{\text{number of incident photons}} \times 100 \end{aligned} \quad (1)$$

### 2.4. Photocatalytic bacterial inactivation

*Escherichia coli* K-12 was chosen as the model bacteria to evaluate the photocatalytic inactivation efficiency of the prepared photocatalysts [40]. Bacterial cells were firstly cultured in Nutrient Broth growth medium at 37 °C for 16 h with shaking, and then harvested by centrifugation at 4000 rpm for 15 min. The bacterial pellets were then washed with sterilized saline (0.9% NaCl) solution three times in a centrifuge tube and re-suspended in a sterilized saline solution to obtain suitable concentration of *E. coli*. Then, 50 mg of the as-prepared photocatalyst was added into 50 mL solution containing  $10^7$  cfu  $\text{mL}^{-1}$  bacterial suspensions. The solution was irradiated by a 300 W Xenon lamp equipped with a 420 nm cut-off filter. Then, at different time intervals, aliquot samples were collected and uniformly spread on Nutrient Agar plates after serial dilutions using the sterilized saline solution. The plates were incubated at 37 °C for 24 h to determine the viable cell count. All the inactivation experiments were conducted in triplicate.

## 3. Results and discussion

### 3.1. Synthesis and characterization of prepared catalyst

Fig. 1 shows the XRD patterns of as-prepared  $\text{Ni}_2\text{P}$ ,  $\text{g-C}_3\text{N}_4$  and  $\text{Ni}_2\text{P}/\text{g-C}_3\text{N}_4$  hybrids with different  $\text{Ni}_2\text{P}$  loading amounts. The  $\text{Ni}_2\text{P}$  sample exhibits obvious diffraction peaks located at 40.8°, 44.6°, 47.3° and 54.2°, which matches well with the standard card of  $\text{Ni}_2\text{P}$

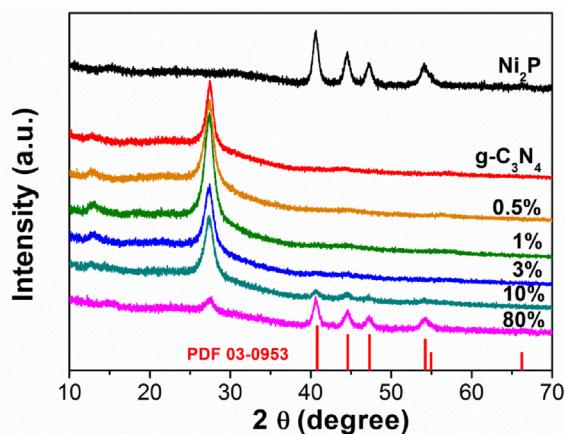
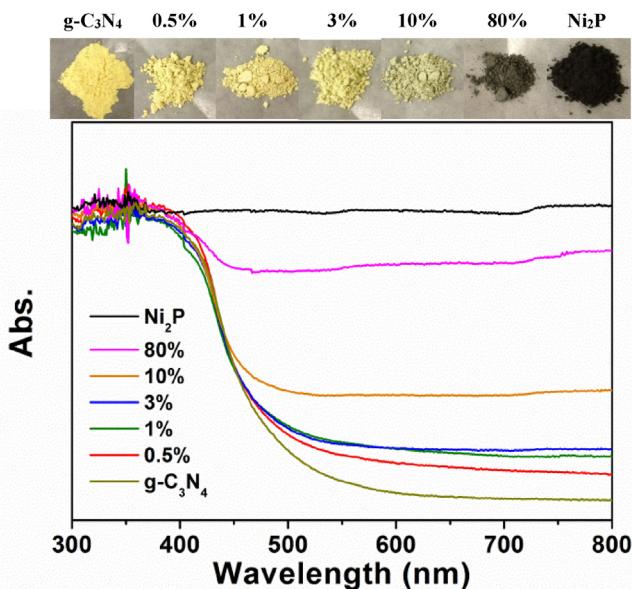


Fig. 1. X-Ray diffraction (XRD) patterns of  $\text{g-C}_3\text{N}_4$ ,  $\text{Ni}_2\text{P}$  and  $\text{Ni}_2\text{P}/\text{g-C}_3\text{N}_4$  lamellar nanohybrids with different  $\text{Ni}_2\text{P}$  loading amount.

(PDF 03-0953), confirming pure  $\text{Ni}_2\text{P}$  crystals can be successfully synthesized at the present hydrothermal condition. Meanwhile, two distinct XRD peaks at 13.0° and 27.4° are observed for pure  $\text{g-C}_3\text{N}_4$  synthesized using melamine as the precursor, which are assigned to the (100) and (002) plane of the typical graphitic layer structures [41]. The peak at 13.0° is related to the in-plane repeating units of the heptazine heteroatom cycles, while the later one is assigned to the graphitic layer stacking, similar in graphite. However, the  $\text{Ni}_2\text{P}/\text{g-C}_3\text{N}_4$  samples exhibit similar XRD pattern with pure  $\text{g-C}_3\text{N}_4$ , and no noticeable change can be found with the  $\text{Ni}_2\text{P}$  loading concentration from 0.5 to 3%, which is due to weak X-ray diffraction intensity of low concentration and highly dispersed  $\text{Ni}_2\text{P}$  nanoparticles. Similar observation was also found in Pt-loaded  $\text{g-C}_3\text{N}_4$  photocatalysts [42,43]. When further increasing the loading concentration to 10 and 80%, the diffraction peaks corresponding to  $\text{Ni}_2\text{P}$  can be gradually observed, indicating the successful introduction of  $\text{Ni}_2\text{P}$  to  $\text{g-C}_3\text{N}_4$  by the facile one-pot hydrothermal synthesis. The intensity of diffraction peak located at 27.4° decreases with the increase of  $\text{Ni}_2\text{P}$  amount. This is due to the increase of  $\text{Ni}_2\text{P}$  diffraction intensity and the decrease of  $\text{g-C}_3\text{N}_4$  crystallinity during the hydrothermal exfoliation process.

To investigate the light harvesting property of  $\text{g-C}_3\text{N}_4$ ,  $\text{Ni}_2\text{P}$ , as well as  $\text{Ni}_2\text{P}/\text{g-C}_3\text{N}_4$  with different mass ratios, UV-vis analysis was performed and the spectra were displayed in Fig. 2. Pure  $\text{g-C}_3\text{N}_4$  show typical semiconductor absorption, originating from charge transfer response of  $\text{g-C}_3\text{N}_4$  from the VB populated by N 2p orbitals to the CB formed by C 2p orbitals. It shows a light absorption edge of approximately 470 nm, corresponding to the band gap energy of 2.64 eV. The tailed light absorption is attributed to the surface defects, leading to inter-band absorption. It is known that  $\text{Ni}_2\text{P}$  has a band gap of approximately 1.0 eV, corresponding to wavelength up to 1240 nm [44]. With the increase of  $\text{Ni}_2\text{P}$  addition, the color of  $\text{g-C}_3\text{N}_4$  is changed from yellow to dark (Fig. 2 upper side), indicating the successful incorporation of  $\text{Ni}_2\text{P}$ . However, the absorption edge of  $\text{g-C}_3\text{N}_4$  is not shifted with the increase of  $\text{Ni}_2\text{P}$  loading amount, but only the absorption intensity is enhanced in the VL region longer than 500 nm. Little change in the light absorption was observed when the  $\text{Ni}_2\text{P}$  loading amount is below 3%, indicating that  $\text{Ni}_2\text{P}$  was tightly deposited onto the surface of  $\text{g-C}_3\text{N}_4$  instead of being doped into the  $\text{g-C}_3\text{N}_4$  lattice.

The molecular structure information of the samples was illustrated by FT-IR spectra, as depicted in Fig. 3(A). With respect to  $\text{g-C}_3\text{N}_4$ , the prominent bands in the region of 1200–1650  $\text{cm}^{-1}$  can be related to the typical stretching modes of CN heterocycles, wherein the peaks at 1241, 1318, and 1425  $\text{cm}^{-1}$  are assigned to the aromatic C–N stretching [45,46]. The sharp band



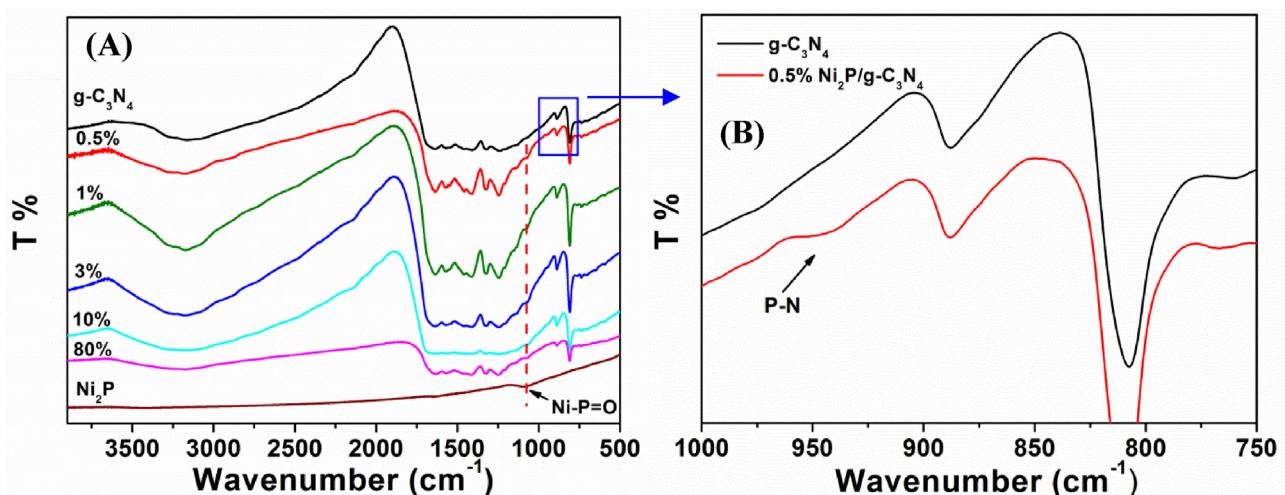
**Fig. 2.** UV-vis diffuse reflectance spectra (UV-vis DRS) of  $\text{g-C}_3\text{N}_4$ ,  $\text{Ni}_2\text{P}$  and  $\text{Ni}_2\text{P}/\text{g-C}_3\text{N}_4$  lamellar nanohybrids with different  $\text{Ni}_2\text{P}$  loading amount.

at  $809\text{ cm}^{-1}$  is attributed to the out-of-plane bending vibration of characteristics of triazine rings [47]. The broad peaks at around  $2600\text{--}3400\text{ cm}^{-1}$  originate from stretching vibration modes for the  $-\text{NH}$  and hydroxyl group of the adsorbed  $\text{H}_2\text{O}$ . The pure  $\text{Ni}_2\text{P}$  shows a broad signal at  $1080\text{ cm}^{-1}$ , which can be assigned to the Ni bound  $\text{P=O}$  stretching band, a natural consequence of surface oxidation in the open air [48]. This observation is similar with the results reported by Carenco et al. [49] and Senevirathne et al. [50]. The FT-IR spectrum of as-prepared  $\text{Ni}_2\text{P}/\text{g-C}_3\text{N}_4$  samples signifies that the typical graphitic structure of carbon nitride was well maintained after hydrothermal reactions, while the characteristic peak corresponding to  $\text{Ni}_2\text{P}$  at  $1080\text{ cm}^{-1}$  was also observed indicating the successful loading of  $\text{Ni}_2\text{P}$  onto  $\text{g-C}_3\text{N}_4$  nanosheets. The vibration band corresponding to P-related functional groups can hardly be observed, except for a weak peak located at approximately  $950\text{ cm}^{-1}$  (Fig. 3(B)), which is assigned to  $\text{P-N}$  stretching mode [51,52]. The peak intensity is low presumably due to the overlapping of the bands with those of strong  $\text{C-N}$  vibrations. These results indicate the  $\text{Ni}_2\text{P}$  was successfully loaded onto  $\text{g-C}_3\text{N}_4$  via

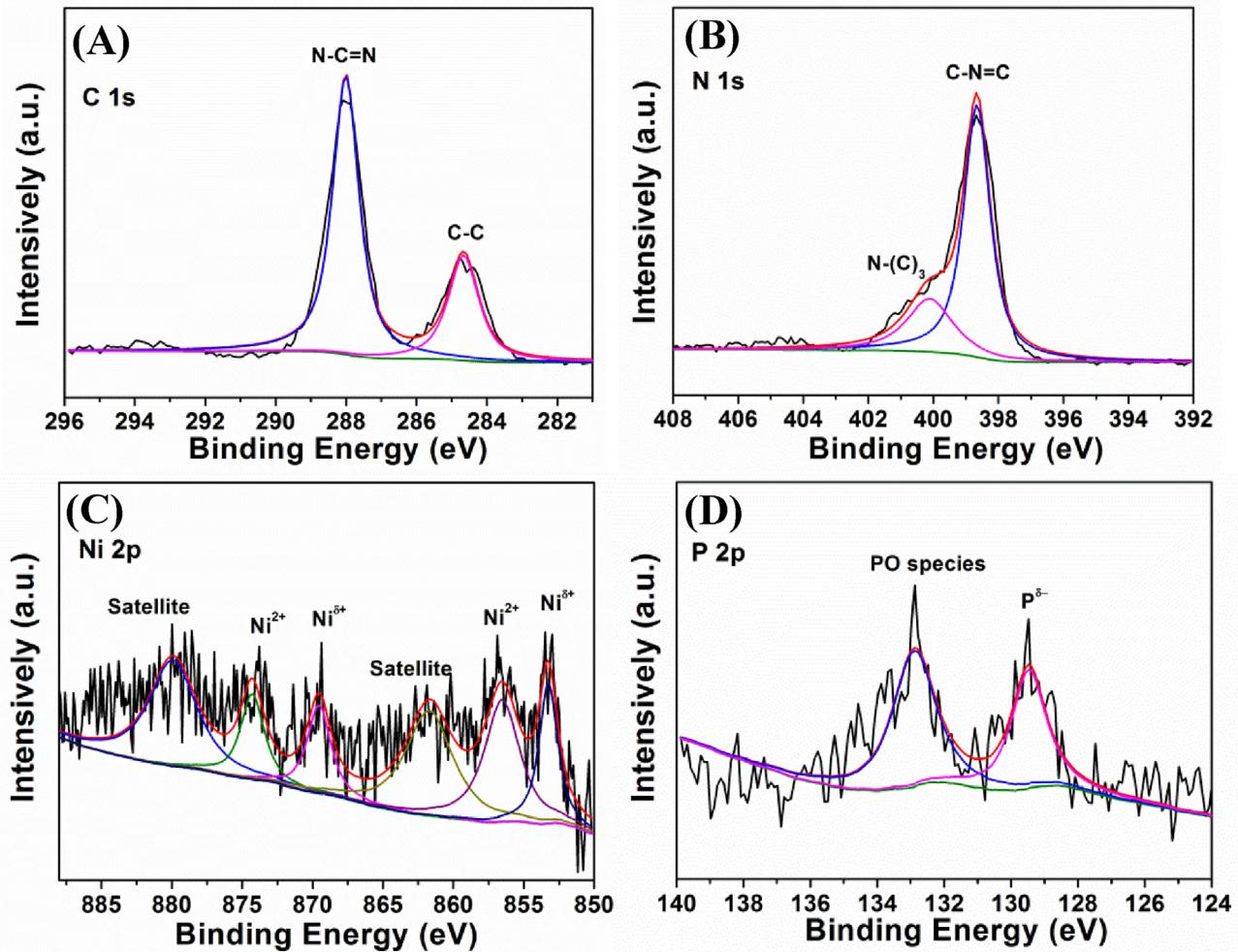
P–N chemical bonding, which offers intimate and direct contact between  $\text{Ni}_2\text{P}$  and  $\text{g-C}_3\text{N}_4$ .

XPS spectra are recorded to analyze the surface species and chemical states of C, N, Ni, and P for typical 1%  $\text{Ni}_2\text{P}/\text{g-C}_3\text{N}_4$ . In high resolution XPS spectrum of C 1s (Fig. 4(A)), two deconvolution peaks at 284.6 and 288.0 eV are observed, which are assigned to graphite C–C bonds and  $\text{sp}^2$ -hybridized carbon in N-containing aromatic ring ( $\text{N}-\text{C}=\text{N}$ ) [53], respectively. The latter is considered as the major carbon species in  $\text{g-C}_3\text{N}_4$ . The high resolution N 1s spectra can be also deconvoluted into two different peaks at binding energies of 398.7 and 400.1 eV (Fig. 4(B)), corresponding to the  $\text{sp}^2$ -hybridized nitrogen involved in triazine rings ( $\text{C}-\text{N}=\text{C}$ ) and the tertiary nitrogen  $\text{N}-(\text{C})_3$  groups, respectively [54]. For the Ni 2p region, three peaks are seen at 853.2, 856.7 and 862.5 eV (Fig. 4(C)), which is ascribed to  $\text{Ni}^{\delta+}$  ( $0 < \delta < 2$ ) in  $\text{Ni}_2\text{P}$ , oxidized Ni species ( $\text{Ni}^{2+}$ ) and the satellite of the  $\text{Ni} 2p_{1/2}$  peak, respectively [55]. In addition, the other three peaks at 869.5, 874.1 and 879.8 eV is corresponding to  $\text{Ni}^{\delta+}$  in  $\text{Ni}_2\text{P}$ , oxidized Ni species and the satellite of the  $\text{Ni} 2p_{3/2}$  peak, respectively [56]. For the P 2p energy level (Fig. 4(D)), the peak at 129.7 eV is a mark of metal–P bonds in metal phosphides (i.e.  $\text{Ni}_2\text{P}$ ) [57], while the peak at 132.9 eV can be attributed to the oxidized P species due to air contact [55]. Because of the low content of  $\text{Ni}_2\text{P}$  loading, the weak XPS signals are observed for Ni 2p and P 2p. These results further confirm the formation of  $\text{Ni}_2\text{P}$  in the hybrids.

The morphologies of as-prepared  $\text{Ni}_2\text{P}/\text{g-C}_3\text{N}_4$  samples were studied by SEM and TEM technology. Fig. 5(A) shows a typical SEM image of 1%  $\text{Ni}_2\text{P}/\text{g-C}_3\text{N}_4$ , exhibiting a lamellar structure of multilayer  $\text{g-C}_3\text{N}_4$  nanosheets. It is found that the  $\text{Ni}_2\text{P}$  spherical nanoparticles are evenly decorated onto the nanosheets. TEM image in Fig. 5(B) further confirms the microstructure of the  $\text{Ni}_2\text{P}/\text{g-C}_3\text{N}_4$  nanosheet hybrids, which demonstrates that it is feasible to achieve the exfoliation of  $\text{g-C}_3\text{N}_4$  while *in-situ* loaded with  $\text{Ni}_2\text{P}$  nanoparticles by the one-pot hydrothermal method. In contrast, the pristine  $\text{g-C}_3\text{N}_4$  clearly shows an unexfoliated large particle morphology (Fig. S1). Moreover, the lattice fringes with a spacing of 0.22 nm are evident in the high-resolution TEM image (Fig. 5(D)). The d spacing can be indexed to the high intense (111) reflection of  $\text{Ni}_2\text{P}$  [58]. The corresponding EDS spectrum in Fig. 5(C) clearly shows the elements of C, N, Ni and P, further confirming the successful formation of  $\text{g-C}_3\text{N}_4$  and  $\text{Ni}_2\text{P}$ . The signals of C and Cu come from the carbon-coated copper grid substrate. The TEM images of  $\text{Ni}_2\text{P}/\text{g-C}_3\text{N}_4$  samples with different  $\text{Ni}_2\text{P}$  loading amount are also presented in Fig. 6. The 0.5%  $\text{Ni}_2\text{P}/\text{g-C}_3\text{N}_4$  shows a



**Fig. 3.** (A) Fourier transform infrared (FT-IR) spectra of  $\text{g-C}_3\text{N}_4$ ,  $\text{Ni}_2\text{P}$  and  $\text{Ni}_2\text{P}/\text{g-C}_3\text{N}_4$  lamellar nanohybrids with different  $\text{Ni}_2\text{P}$  loading amount; (B) Enlarged area in plane (A).



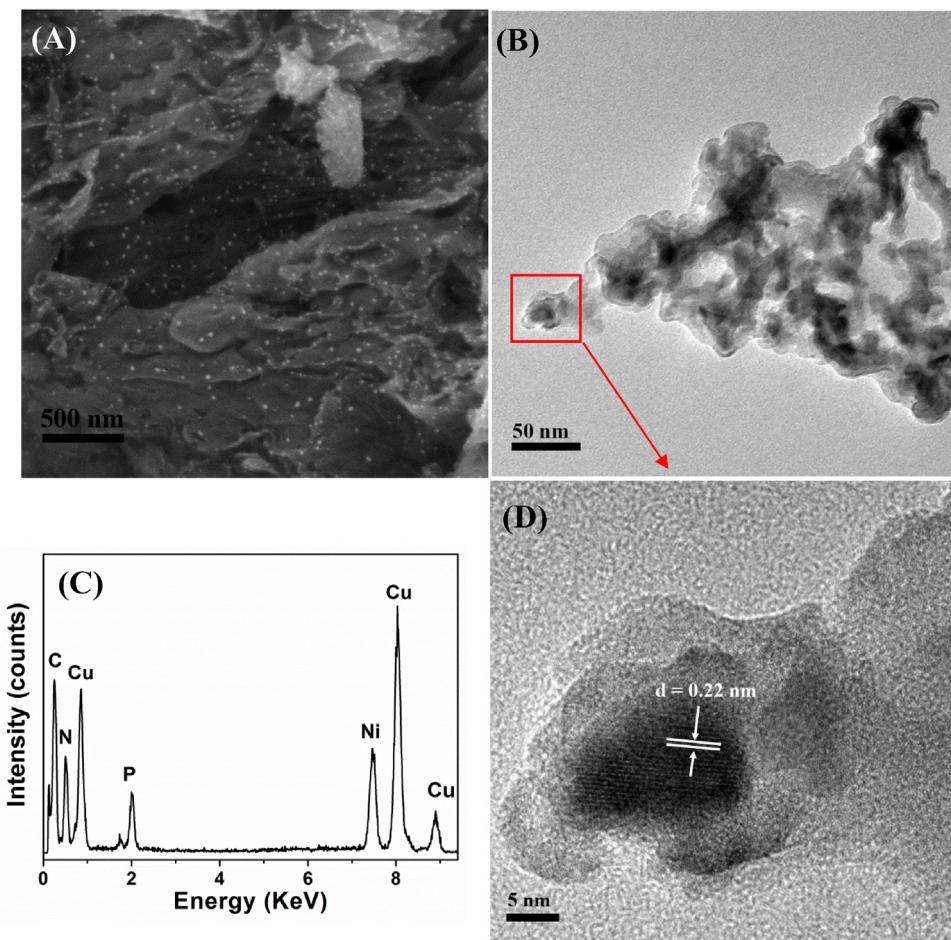
**Fig. 4.** High resolution X-ray photoelectron spectroscopy (XPS) spectra of 1% Ni<sub>2</sub>P/g-C<sub>3</sub>N<sub>4</sub> sample: (A) C 1s; (B) N 1s; (C) Ni 2p; (d) P 2p.

clear lamellar morphology with tiny Ni<sub>2</sub>P nanoparticles (Fig. 6(A)), indicating small amount of Ni<sup>2+</sup> is enough to help exfoliating the g-C<sub>3</sub>N<sub>4</sub>. With increasing Ni<sub>2</sub>P content, the Ni<sub>2</sub>P nanoparticles with sizes of 10–50 nm grow bigger and gradually are aggregated together (Fig. 6(B-E)). It is found that high amount of Ni<sup>2+</sup> addition (>10% Ni<sub>2</sub>P) would result in the deterioration of g-C<sub>3</sub>N<sub>4</sub> exfoliation efficiency, leading to the formation of unexfoliated Ni<sub>2</sub>P/g-C<sub>3</sub>N<sub>4</sub> aggregates, which is unfavorable for photocatalytic reactions.

Based on the above results, the exfoliation of g-C<sub>3</sub>N<sub>4</sub> and its induced *in-situ* anchoring of Ni<sub>2</sub>P synthesis process is illustrated in Fig. 7. At the initial stage, the divalent nickel ions with ionic radius of approximately 0.07 nm are inserted into the layered g-C<sub>3</sub>N<sub>4</sub> material. Subsequently, the inserted Ni<sup>2+</sup> cations react with red P to produce Ni<sub>2</sub>P nucleus, which then undergo slow heterogeneous nucleation, restricted growth and finally come into being crystalline Ni<sub>2</sub>P nanoparticles anchored onto the layered g-C<sub>3</sub>N<sub>4</sub>, and this process in turn promotes the self-exfoliation of bulk g-C<sub>3</sub>N<sub>4</sub>, resulting in *in-situ* fabrication of lamellar Ni<sub>2</sub>P/g-C<sub>3</sub>N<sub>4</sub> nanohybrids. To further prove this mechanism, hydrothermal treatment of bulk g-C<sub>3</sub>N<sub>4</sub> without Ni<sup>2+</sup> addition was also conducted, and the results show that only particles of g-C<sub>3</sub>N<sub>4</sub> can be obtained (Fig. S2), confirming the crucial role of Ni<sup>2+</sup> for the exfoliation of g-C<sub>3</sub>N<sub>4</sub>. This Ni<sup>2+</sup>-induced exfoliation mechanism is expected to find applications for exfoliating other lamellar materials, especially for simultaneous anchoring with Ni species.

### 3.2. Photocatalytic H<sub>2</sub> evolution performances

The photocatalytic hydrogen production activities of the as-prepared samples were evaluated with TEOA as a sacrificial agent under visible light irradiation. Fig. 8(A) shows the H<sub>2</sub> evolution activity of Ni<sub>2</sub>P/g-C<sub>3</sub>N<sub>4</sub> lamellar nanohybrid photocatalysts with different loading amounts of Ni<sub>2</sub>P. Notably, the yield of H<sub>2</sub> increases linearly with increasing reaction time over all the Ni<sub>2</sub>P/g-C<sub>3</sub>N<sub>4</sub> samples. The H<sub>2</sub> evolution efficiency is calculated and shown in Fig. 8(B). Pure g-C<sub>3</sub>N<sub>4</sub> and Ni<sub>2</sub>P nanoparticles are used for the comparison. No appreciable H<sub>2</sub> is observed when Ni<sub>2</sub>P alone is used under visible light irradiation, revealing that Ni<sub>2</sub>P is not an active photocatalyst for H<sub>2</sub> evolution, probably due to its small band gap (1.0 eV). The g-C<sub>3</sub>N<sub>4</sub> shows little photocatalytic activity for H<sub>2</sub> evolution ( $\sim 16.4 \mu\text{mol h}^{-1} \text{g}^{-1}$ ) without noble metal loading, which is in agreement with previous studies that noble metal loading is indispensable for g-C<sub>3</sub>N<sub>4</sub> photocatalytic system [59]. Interestingly, with only 0.5% of Ni<sub>2</sub>P loaded on g-C<sub>3</sub>N<sub>4</sub> to produce Nanohybrid, the Ni<sub>2</sub>P/g-C<sub>3</sub>N<sub>4</sub> photocatalysts exhibits a significantly enhanced H<sub>2</sub> evolution rate of  $169.1 \mu\text{mol h}^{-1} \text{g}^{-1}$ . With increasing loading amounts of Ni<sub>2</sub>P, the H<sub>2</sub> evolution rate is increased accordingly. The highest photocatalytic H<sub>2</sub> evolution rate is achieved with 1% Ni<sub>2</sub>P loading, providing an extraordinary H<sub>2</sub> evolution rate of  $362.4 \mu\text{mol h}^{-1} \text{g}^{-1}$ , which is approximately 22 times higher than that of g-C<sub>3</sub>N<sub>4</sub> alone. However, further increasing the content of Ni<sub>2</sub>P would result in the decrease of the photocatalytic activity. It is found that the H<sub>2</sub> evolution rate is gradually reduced to 248.8,



**Fig. 5.** (A) Typical scanning electron microscopy (SEM) image, (B) Transmission electron microscopy (TEM) image, (C) Energy-dispersive X-ray (EDX) spectrum and (D) High resolution transmission electron microscopy (HRTEM) image of 1% Ni<sub>2</sub>P/g-C<sub>3</sub>N<sub>4</sub>.

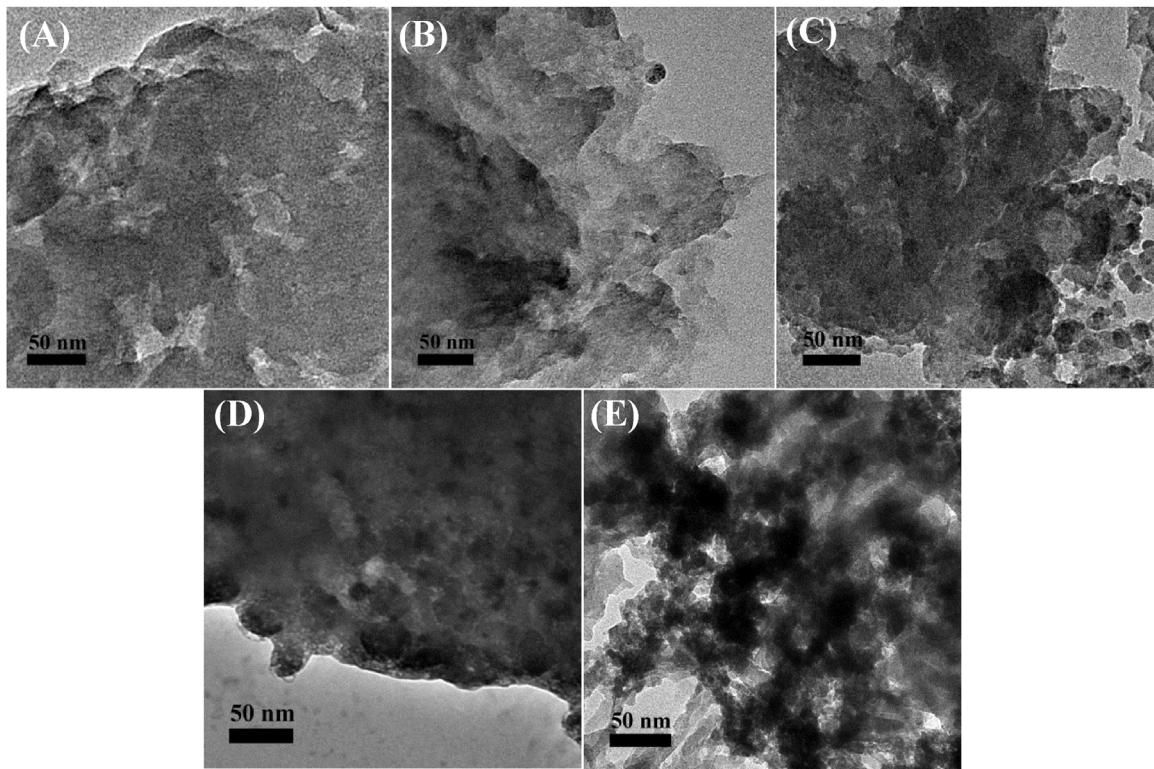
175.2 and 35.2  $\mu\text{mol h}^{-1} \text{g}^{-1}$  for the samples with 3, 10 and 80% Ni<sub>2</sub>P loading, respectively.

As known, Pt is the most commonly used noble metal co-catalyst to enhance the H<sub>2</sub> evolution activity. Therefore, the photocatalytic H<sub>2</sub> evolution activity of 1% Pt/g-C<sub>3</sub>N<sub>4</sub> was measured to compare with 1% Ni<sub>2</sub>P/g-C<sub>3</sub>N<sub>4</sub> under the same reaction conditions. The results show that the H<sub>2</sub> evolution amount increases linearly with time in both systems of Pt/g-C<sub>3</sub>N<sub>4</sub> and Ni<sub>2</sub>P/g-C<sub>3</sub>N<sub>4</sub>, while the Ni<sub>2</sub>P/g-C<sub>3</sub>N<sub>4</sub> exhibits obvious higher rate than that of Pt/g-C<sub>3</sub>N<sub>4</sub> (Fig. S3), demonstrating that Ni<sub>2</sub>P is a good noble-metal-free co-catalyst coupled with g-C<sub>3</sub>N<sub>4</sub> under visible light irradiation. The apparent quantum efficiency (AQE) at 420 nm was evaluated by measuring the H<sub>2</sub> production rate under monochromatic light ( $\lambda = 420 \text{ nm}$ ) irradiation. The calculated AQE is approximately 1.8% and maintains stable for 6 h of visible light irradiation (Fig. S4). It was found the value was lower in the first hour (1.57%), which may be due to an induction period at the early stages and the dissolved H<sub>2</sub> in the solution [60]. Moreover, the wavelength dependence of photocatalytic H<sub>2</sub> evolution was also investigated in the range of 420–550 nm using various band pass filters ( $\lambda = 420, 450, 500$  and 550 nm). As shown in Figs. 8(C) and S5, the photocatalytic H<sub>2</sub> production rate under different wavelengths matches very well with its light absorption property, indicating the H<sub>2</sub> evolution is indeed a light-induced catalytic reactions. Notably, the longest wavelength used for H<sub>2</sub> evolution is extended to 550 nm, which is attributed to the efficient electron trapping ability of Ni<sub>2</sub>P as the co-catalysts. In addition, the photo-stability was also evaluated by performing recycling experiments. As shown in Fig. 8(D), the H<sub>2</sub> evolution

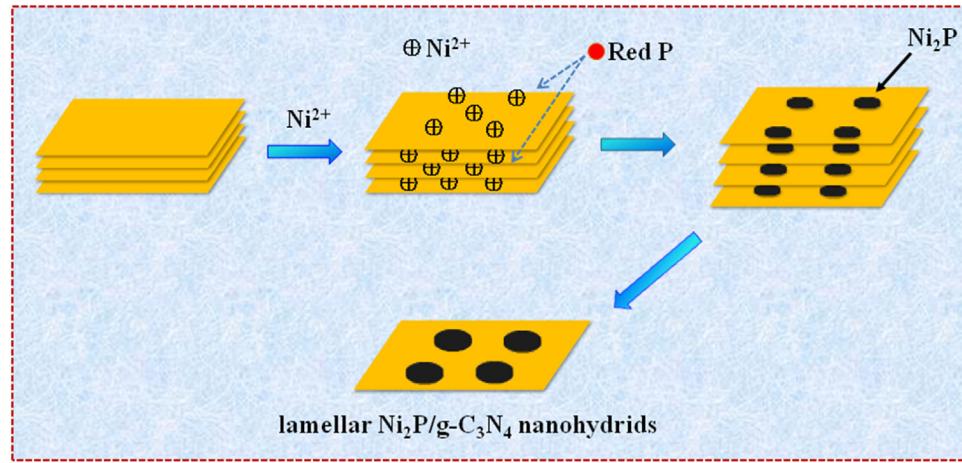
yield remains unchanged after five runs under visible light irradiation (total for 30 h), confirming the sufficient stability of hybrid Ni<sub>2</sub>P/g-C<sub>3</sub>N<sub>4</sub> catalyst for photocatalytic H<sub>2</sub> evolution.

### 3.3. Photocatalytic bacterial inactivation performances

The photocatalytic disinfection activity was also evaluated by inactivating *E. coli* K-12 as a representative waterborne microorganism. As shown in Fig. 9(A), the g-C<sub>3</sub>N<sub>4</sub> and Ni<sub>2</sub>P nanoparticles shows similar bacterial inactivation activity, and less than 2.5-log cfu mL<sup>-1</sup> *E. coli* K-12 can be inactivated within 4 h of visible light irradiation. Interestingly, with only 0.5% Ni<sub>2</sub>P loading, the as-prepared Ni<sub>2</sub>P/g-C<sub>3</sub>N<sub>4</sub> sample exhibits obvious enhanced photocatalytic bacterial inactivation activity (3-log cfu mL<sup>-1</sup> cell reduction within 4 h), and the inactivation efficiency is found to further increase with the increase of Ni<sub>2</sub>P loading amount. The highest activity is observed from 10% Ni<sub>2</sub>P/g-C<sub>3</sub>N<sub>4</sub> photocatalyst, on which total 7-log cfu mL<sup>-1</sup> cell reduction is completely achieved within 4 h. The photocatalytic bacterial inactivation activity of 10% Ni<sub>2</sub>P/g-C<sub>3</sub>N<sub>4</sub> is compared with that of 10% Pt/g-C<sub>3</sub>N<sub>4</sub>. The results show that only approximately 3.5-log cfu mL<sup>-1</sup> cell reduction is obtained with Pt/g-C<sub>3</sub>N<sub>4</sub> under the same condition (Fig. S6), indicating the Ni<sub>2</sub>P/g-C<sub>3</sub>N<sub>4</sub> also shows much higher photocatalytic bacterial inactivation activity than that of Pt/g-C<sub>3</sub>N<sub>4</sub>. It is obvious that the intimate heterojunctions between g-C<sub>3</sub>N<sub>4</sub> and Ni<sub>2</sub>P play the important role in determining the high photocatalytic activity. It is also noted that no bacterial cells are inactivated in light control experiments, while a very slight reduction of cell density in dark with 10% Ni<sub>2</sub>P/g-C<sub>3</sub>N<sub>4</sub>



**Fig. 6.** Transmission electron microscopy (TEM) images of lamellar Ni<sub>2</sub>P/g-C<sub>3</sub>N<sub>4</sub> nanohybrids with different Ni<sub>2</sub>P loading amount: (A) 0.5%; (B) 1%; (C) 3%; (D) 10%, (E) 80%.



**Fig. 7.** Schematic illustration of the formation process of lamellar Ni<sub>2</sub>P/g-C<sub>3</sub>N<sub>4</sub> nanohybrids.

is observed, probably due to the intrinsic antibacterial property or the adsorption of Ni<sub>2</sub>P nanoparticles.

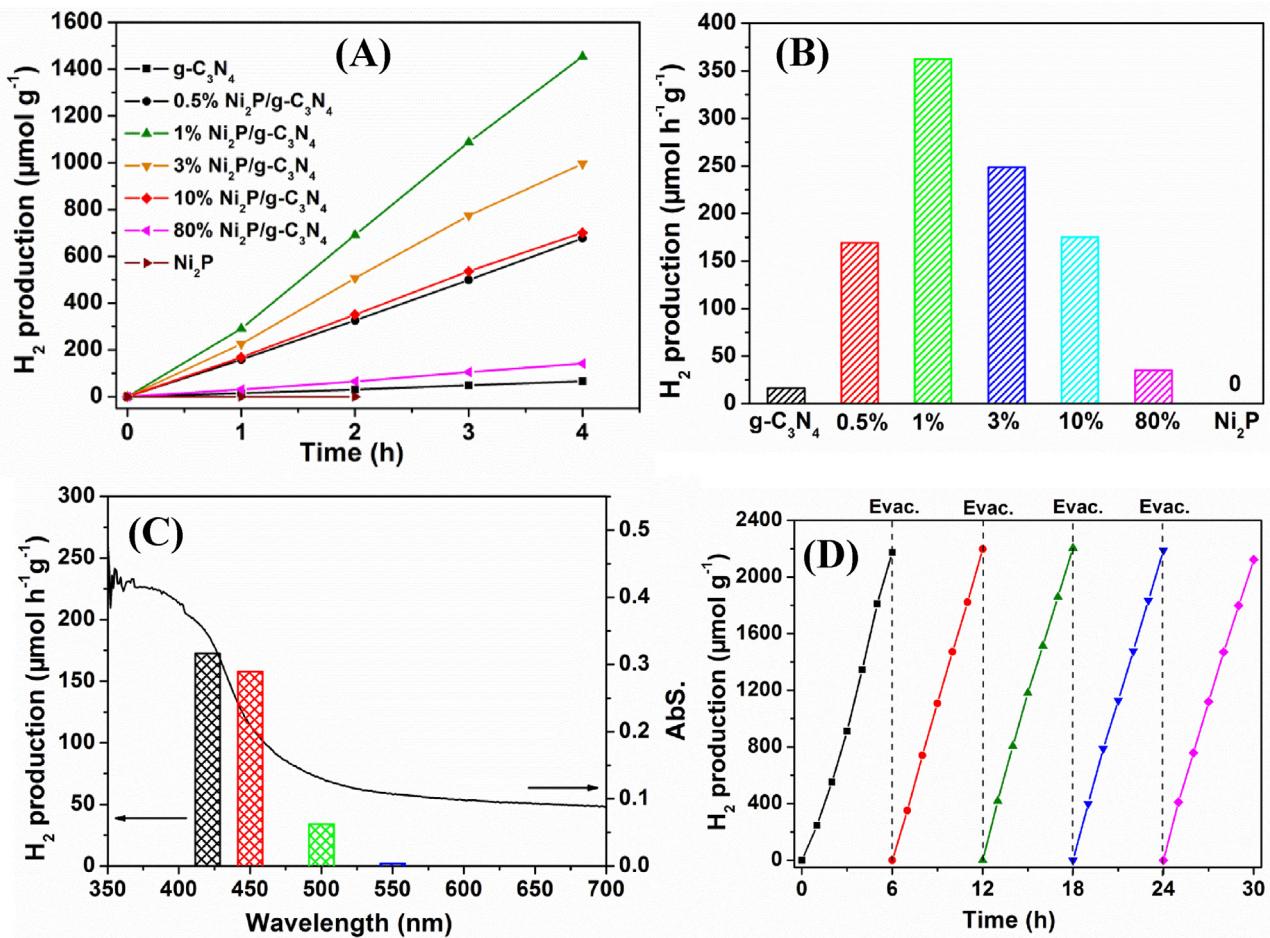
To quantitatively understand the reaction rate, the inactivation kinetics were also modeled with a first-order decay of viability, followed by the presence of a tailing phase in which liberated intracellular components competing with the intact cell for the photocatalytic attack. These results were fitted well ( $R^2 = 0.99$ ) using the model proposed by Geeraerd et al. [61] (Eq. (2)):

$$N_t = (N_0 - N_{\text{res}}) \times \exp(-k_{\text{max}} \times t) + N_{\text{res}} \quad (2)$$

Where  $N_t$  and  $N_0$  was the survival number of cells at reaction time ( $t$ ) and initial time, respectively;  $k_{\text{max}}$  denoted the inactivation rate and  $N_{\text{res}}$  was the residual number of the cells, and the fitted  $k_{\text{max}}$  values are shown in Fig. 9(B). The pure g-C<sub>3</sub>N<sub>4</sub> and Ni<sub>2</sub>P nanoparticles show a  $k_{\text{max}}$  value of only 0.07 and 0.13, respec-

tively. With the increase of Ni<sub>2</sub>P loading amount, the  $k_{\text{max}}$  values increases from 0.53 to 0.71, and then decreases to 0.63 for 80% Ni<sub>2</sub>P/g-C<sub>3</sub>N<sub>4</sub>. Therefore, the 10% Ni<sub>2</sub>P/g-C<sub>3</sub>N<sub>4</sub> exhibits significantly enhanced photocatalytic bacterial inactivation efficiency by a factor of at least 10 times higher than that of pure g-C<sub>3</sub>N<sub>4</sub>. It is noted that the optimal Ni<sub>2</sub>P loading amount for H<sub>2</sub> evolution is 1%, while this is 10% for bacterial inactivation. The difference can be rationalized by considering the intrinsic antibacterial property of Ni<sub>2</sub>P, which contribute to the bacterial inactivation efficiency but not for H<sub>2</sub> evolution. Therefore, with more Ni<sub>2</sub>P loading beyond 1%, the bacterial inactivation efficiency can be further improved, and the optimal amount of Ni<sub>2</sub>P increases to 10%.

To understand the bacterial inactivation mechanism during the photocatalytic process, scavenging studies was conducted by using isopropanol, Cr(VI), Fe(II)-EDTA and oxalate as •OH, e<sup>-</sup>, H<sub>2</sub>O<sub>2</sub> and



**Fig. 8.** (A) Photocatalytic H<sub>2</sub> evolution by as-prepared samples under VL irradiation; (B) Normalized H<sub>2</sub> evolution rate within 4 h; (C) Wavelength-dependent photocatalytic H<sub>2</sub> evolution over 1% Ni<sub>2</sub>P/g-C<sub>3</sub>N<sub>4</sub> under different monochromatic light irradiation; (D) Cyclic H<sub>2</sub> evolution curve for 1% Ni<sub>2</sub>P/g-C<sub>3</sub>N<sub>4</sub> sample under VL irradiation.

h<sup>+</sup> scavengers, respectively, with the method recommended by the reference [62]. No bacterial inactivation was observed with the addition of these scavengers (Fig. S7), indicating the present dosage of scavengers would not cause detectable toxicity to the bacterial cells. As shown in Fig. 9(C), the addition of isopropanol and Cr(VI) has little influence on the photocatalytic bacterial inactivation efficiency, indicating the •OH and e<sup>-</sup> are not directly involved in the inactivation process. With the addition of Fe(II)-EDTA, the inactivation efficiency is decreased significantly, suggesting H<sub>2</sub>O<sub>2</sub> is important for the inactivation in this system. However, the addition of oxalate almost completely inhibits the inactivation process, which indicates that the h<sup>+</sup> may be the major reactive species for the bacterial inactivation, and the H<sub>2</sub>O<sub>2</sub> is produced from h<sup>+</sup> at the valence band of g-C<sub>3</sub>N<sub>4</sub> [40,63]. To evaluate the photocatalytic stability, the bacterial inactivation treatment was also repeated five times with the same 10% Ni<sub>2</sub>P/g-C<sub>3</sub>N<sub>4</sub> sample (Fig. 9(D)). Results showed that no obvious deterioration of inactivation efficiency was observed in the first four runs, confirming the high photo-stability of Ni<sub>2</sub>P/g-C<sub>3</sub>N<sub>4</sub> although there was a slight decrease in inactivation efficiency in the fifth run, probably due to the loss of catalysts during the repeated cycling experiments.

### 3.4. Photocatalytic mechanisms

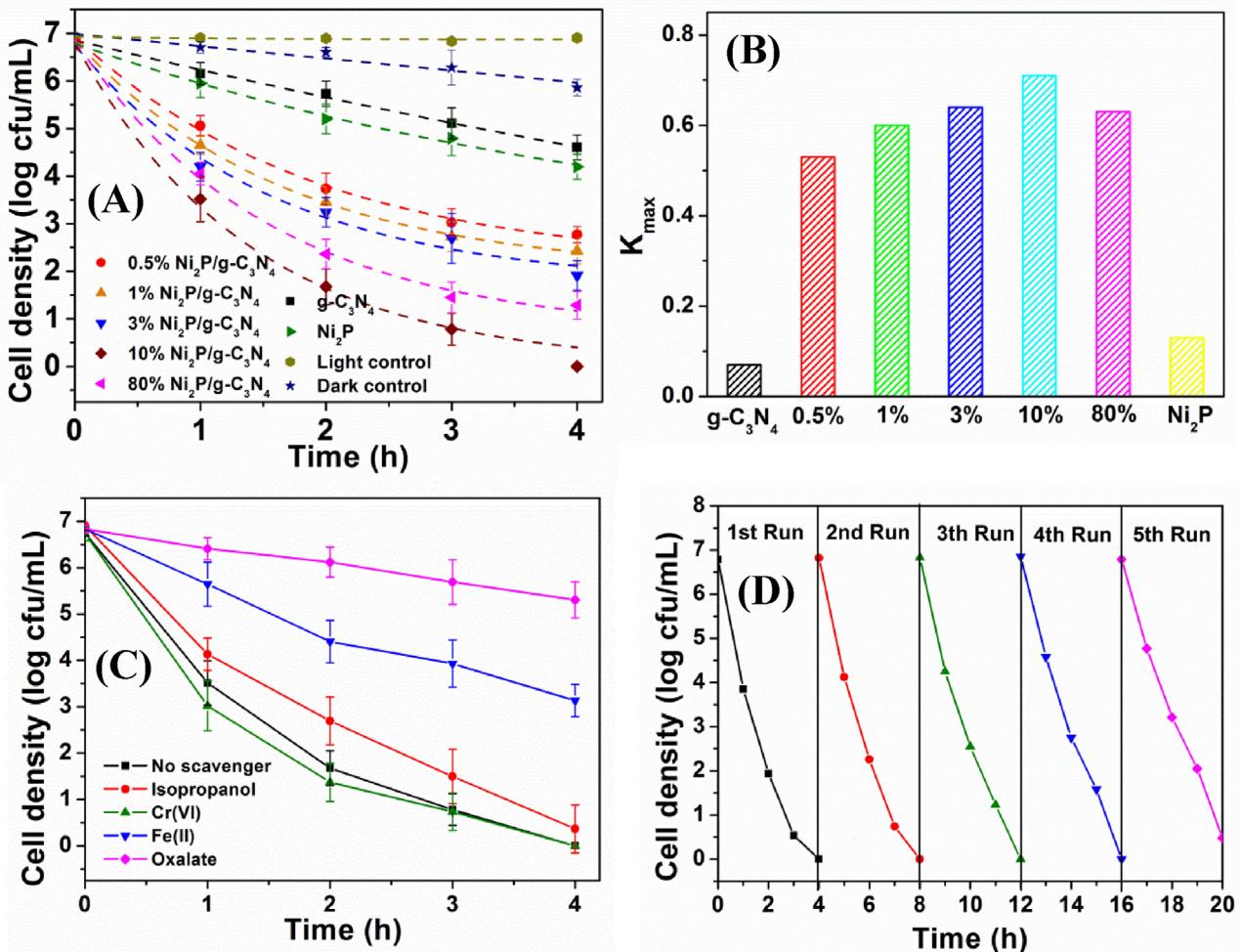
To understand the effects of Ni<sub>2</sub>P loading on the photo-generated e<sup>-</sup>-h<sup>+</sup> separation, migration and transfer during the photocatalytic process, the band structures of g-C<sub>3</sub>N<sub>4</sub> and Ni<sub>2</sub>P were studied. It is generally known that the conduction band (CB)

and valence band (VB) potentials designated as E<sub>CB</sub> and E<sub>VB</sub> can be estimated according to the following empirical Eqs. (3) and (4):

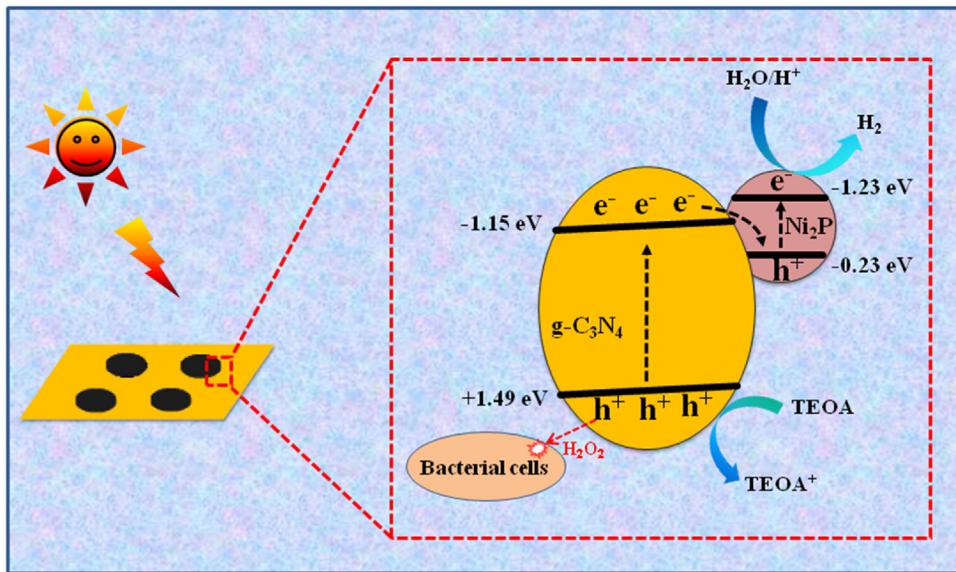
$$E_{CB} = E_{VB} - E_g \quad (3)$$

$$E_{VB} = X - E_e + 0.5E_g \quad (4)$$

Where the E<sub>g</sub>, X and E<sub>e</sub> are the band gap energy, absolute electronegativity of the semiconductor and the energy of free electrons on the hydrogen scale (approximately 4.5 eV), respectively [64,65]. Based on the result of UV-vis spectra, the g-C<sub>3</sub>N<sub>4</sub> has band gap energies of 2.64 eV, while the Ni<sub>2</sub>P has a band gap of 1.0 eV [44]. According to the calculations, the CB and VB potentials of g-C<sub>3</sub>N<sub>4</sub> are approximately -1.15 and 1.49 eV, while the CB and VB potentials of Ni<sub>2</sub>P are approximately -1.23 and -0.23 eV, respectively. As shown in Fig. 10, The CB of g-C<sub>3</sub>N<sub>4</sub> is more positive than that of Ni<sub>2</sub>P while more negative than the VB of Ni<sub>2</sub>P, thus allowing photogenerated electrons excited from the VB of g-C<sub>3</sub>N<sub>4</sub> could subsequently transfer to the VB of Ni<sub>2</sub>P under visible light illumination, forming a Z-scheme type of electron transportation. The SEM and TEM results confirm the intimate contact of Ni<sub>2</sub>P and g-C<sub>3</sub>N<sub>4</sub> in the Ni<sub>2</sub>P/g-C<sub>3</sub>N<sub>4</sub> nanohybrid, which facilitates the efficient transfer of photogenerated carriers. The Ni<sub>2</sub>P acts as the electron sinker and promoter which traps the photogenerated e<sup>-</sup> from g-C<sub>3</sub>N<sub>4</sub>, and promotes the electron energy level, so that H<sub>2</sub>O/H<sup>+</sup> can be more easily to be reduced. In addition, the excellent electrochemical proton reduction property of Ni<sub>2</sub>P as well as the weak binding property of hydrogen on Ni<sub>2</sub>P surface also reduces the energy cost for hydrogen evolution [66]. On the other hand, since the major reactive species



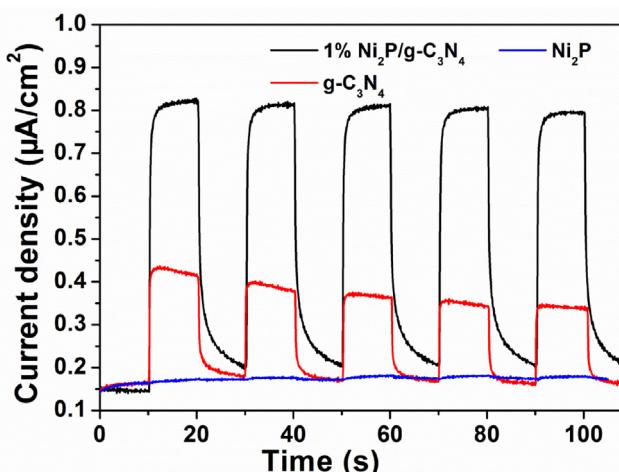
**Fig. 9.** (A) Photocatalytic inactivation efficiencies against *E. coli* K-12 by as-prepared samples with kinetic modeling; (B) Fitted reaction rate constant  $K_{\max}$ ; (C) Photocatalytic inactivation efficiencies against *E. coli* K-12 by as-prepared samples with different scavengers (0.05 mM Cr(VI), 0.5 mM isopropanol, 0.5 mM sodium oxalate, 0.1 mmol/L Fe(II)-EDTA); (D) Recycling experiments of photocatalytic inactivation against *E. coli* K-12 by 10% Ni<sub>2</sub>P/g-C<sub>3</sub>N<sub>4</sub> under VL irradiation.



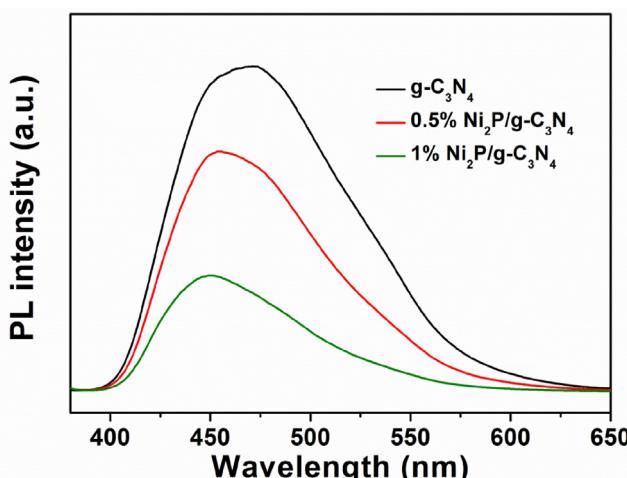
**Fig. 10.** Schematic illustration of the photocatalytic mechanisms of Ni<sub>2</sub>P/g-C<sub>3</sub>N<sub>4</sub> lamellar nanohybrids in H<sub>2</sub> evolution and bacteria inactivation.

for bacterial inactivation in this case is photo-generated  $h^+$ , the excellent electron trapping property of Ni<sub>2</sub>P favors the suppression

of  $e^- - h^+$  recombination, thus more  $h^+$  can be used for bacterial inactivation, which endows the Ni<sub>2</sub>P to be a good co-catalysts for



**Fig. 11.** Transient photocurrent responses of  $\text{g-C}_3\text{N}_4$ ,  $\text{Ni}_2\text{P}$  and 1%  $\text{Ni}_2\text{P}/\text{g-C}_3\text{N}_4$ .



**Fig. 12.** Photoluminescence spectra of  $\text{g-C}_3\text{N}_4$ , 0.5% and 1%  $\text{Ni}_2\text{P}/\text{g-C}_3\text{N}_4$  lamellar nanohybrids excited at 375 nm.

photocatalytic bacterial inactivation. The similar results was also obtained from our early two references that the  $\text{h}^+$  from the VB of  $\text{g-C}_3\text{N}_4$  really can be successfully applied in the transformation of emerging contaminants and the inactivation of bacteria [67,68].

To reveal the migration, transfer and recombination processes of photogenerated  $\text{e}^-$ - $\text{h}^+$  pairs in semiconductors, the photoelectrochemical experiments were conducted and the photocurrent response was also measured. As shown in Fig. 11, the photocurrent responses for the  $\text{Ni}_2\text{P}/\text{g-C}_3\text{N}_4$  composite electrode is prompt, steady and reproducible during repeated on/off cycles of the visible light illumination. The  $\text{g-C}_3\text{N}_4$  shows moderate photocurrent intensity, while the photocurrent is significantly increased with the loading of 1%  $\text{Ni}_2\text{P}$ , suggesting the enhanced migration efficiency of photo-induced charge carriers. Moreover, the charge separation efficiency was further examined by photoluminescence (PL) technique reported from the reference [69]. Fig. 12 presents the photoluminescence spectra of pure  $\text{g-C}_3\text{N}_4$  and  $\text{Ni}_2\text{P}/\text{g-C}_3\text{N}_4$  lamellar nanohydrd. The excitation wavelength of  $\text{g-C}_3\text{N}_4$  is 375 nm according to the previous reference [39]. The strong and wide PL emission peak of  $\text{g-C}_3\text{N}_4$  is clearly decreased after loading only 0.5%  $\text{Ni}_2\text{P}$  co-catalyst, followed by further decreasing with 1%  $\text{Ni}_2\text{P}$  loading, indicating that the recombination of electrons and holes is hindered significantly with increasing  $\text{Ni}_2\text{P}$  loading amount. These results confirm that the incorporation of  $\text{Ni}_2\text{P}$  as co-catalysts could

effectively facilitates the electron–hole separation, migration and transfer at the catalyst interfaces, thus finally enhancing the photocatalytic efficiency of both  $\text{H}_2$  evolution and bacterial inactivation.

#### 4. Conclusions

In summary,  $\text{Ni}_2\text{P}$ -loaded  $\text{g-C}_3\text{N}_4$  lamellar nanohydrd photocatalysts were successfully synthesized by a one-step hydrothermal method based on Z-scheme type of electron transportation model. The exfoliation of  $\text{g-C}_3\text{N}_4$ , the formation and *in-situ* anchoring of  $\text{Ni}_2\text{P}$  nanocrystals onto  $\text{g-C}_3\text{N}_4$  nanosheet were achieved simultaneously without adding any surfactants or template, which is easy to scale up for practical applications. The  $\text{Ni}_2\text{P}$  was loaded onto  $\text{g-C}_3\text{N}_4$  via P-N chemical bonding, offering intimate contact between  $\text{Ni}_2\text{P}$  and  $\text{g-C}_3\text{N}_4$  nanosheet. The as-prepared  $\text{Ni}_2\text{P}/\text{g-C}_3\text{N}_4$  showed much enhanced photocatalytic activity in  $\text{H}_2$  evolution without noble metal loading, with 22 times efficiencies higher than that of  $\text{g-C}_3\text{N}_4$  nanosheets. In addition, it also exhibited enhanced photocatalytic bacterial inactivation activity by a factor of 10 times under visible light irradiation. Thus  $\text{Ni}_2\text{P}$  could effectively trap the photogenerated  $\text{e}^-$  via a Z-scheme type of route, and significantly promoting the  $\text{e}^-$ - $\text{h}^+$  separation and subsequent reduction of protons to generate  $\text{H}_2$ . The efficient trapping of  $\text{e}^-$  would in turn promote the  $\text{h}^+$  accumulation in the VB for bacterial inactivation, making the  $\text{Ni}_2\text{P}/\text{g-C}_3\text{N}_4$  a good bacterial inactivation photocatalysts. Most importantly, this reaction system made of earth-abundant elements would serve as a typical example for constructing “green” and environmental friendly catalysts, thus solving both the energy crisis and environmental pollution problems in a cost-effective and sustainable manner.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [10.1016/j.apcatb.2017.06.027](https://doi.org/10.1016/j.apcatb.2017.06.027).

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